

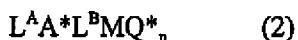
that is bonded to M. In one embodiment of Formula 1 only one of either L^A or L^B is present.

[00118] Independently, each L^A and L^B may be unsubstituted or substituted with a combination of substituent groups R*. Non-limiting examples of substituent groups R* include one or more from the group selected from hydrogen, or linear or branched alkyl radicals, alkenyl radicals, alkynyl radicals, cycloalkyl radicals, aryl radicals, acyl radicals, aroyl radicals, alkoxy radicals, aryloxy radicals, alkylthio radicals, dialkylamino radicals, alkoxy carbonyl radicals, aryloxycarbonyl radicals, carbomoyl radicals, alkyl- or dialkyl-carbamoyl radicals, acyloxy radicals, acylamino radicals, aroylamino radicals or combination thereof. In a preferred embodiment, substituent groups R* have up to 50 non-hydrogen atoms, preferably from 1 to 30 carbon, that can also be substituted with halogens or heteroatoms or the like. Non-limiting examples of alkyl substituents R* include methyl, ethyl, propyl, butyl, pentyl, hexyl, cyclopentyl, cyclohexyl, benzyl or phenyl groups and the like, including all their isomers, for example tertiary butyl, isopropyl, and the like. Other hydrocarbyl radicals include fluoromethyl, fluoroethyl, difluoroethyl, iodopropyl, bromohexyl, chlorobenzyl and hydrocarbyl substituted organometalloid radicals including trimethylsilyl, trimethylgermyl, methyldiethylsilyl and the like; and halocarbyl-substituted organometalloid radicals including tris(trifluoromethyl)silyl, methyl-bis(difluoromethyl)silyl, bromomethyldimethylgermyl and the like; and disubstituted boron radicals including dimethylboron for example; and disubstituted pnictogen radicals including dimethylamine, dimethylphosphine, diphenylamine, methylphenylphosphine, chalcogen radicals including methoxy, ethoxy, propoxy, phenoxy, methylsulfide and ethylsulfide. Non-hydrogen substituents R* include the atoms carbon, silicon, boron, aluminum, nitrogen, phosphorous, oxygen, tin, sulfur, germanium and the like, including olefins such as but not limited to olefinically unsaturated substituents including vinyl-terminated ligands, for example but-3-enyl, prop-2-enyl, hex-5-enyl and the like.

Also, at least two R* groups, preferably two adjacent R groups, are joined to form a ring structure having from 3 to 30 atoms selected from carbon, nitrogen, oxygen, phosphorous, silicon, germanium, aluminum, boron or a combination thereof.

Also, a substituent group, R*, may also be a diradical bonded to L at one end and forming a carbon sigma bond to the metal M. Other ligands may be bonded to the metal M, such as at least one leaving group Q*. In one embodiment, Q* is a monoanionic labile ligand having a sigma-bond to M. Depending on the oxidation state of the metal, the value for n is 0, 1 or 2 such that Formula 1 above represents a neutral bulky ligand metallocene catalyst compound. Non-limiting examples of Q* ligands include weak bases such as amines, phosphines, ethers, carboxylates, dienes, hydrocarbyl radicals having from 1 to 20 carbon atoms, hydrides or halogens and the like or a combination thereof. In another embodiment, two or more Q*'s form a part of a fused ring or ring system. Other examples of Q* ligands include those substituents for R* as described above and including cyclobutyl, cyclohexyl, heptyl, toyl, trifluoromethyl, tetramethylene (both Q*), pentamethylene (both Q*), methylidene (both Q*), methoxy, ethoxy, propoxy, phenoxy, bis(N-methylanilide), dimethylamide, dimethylphosphide radicals and the like.

[00119] In another embodiment, the catalyst composition useful in the invention may include one or more bulky ligand metallocene catalyst compounds where L^A and L^B of Formula 1 are bridged to each other by at least one bridging group, A*, as represented by Formula 2.



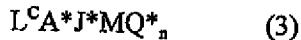
[00120] The compounds of Formula 2 are known as bridged, bulky ligand metallocene catalyst compounds. L^A, L^B, M, Q* and n are as defined above. Non-limiting examples of bridging group A* include bridging groups containing at least one Group 13 to 16 atom, often referred to as a divalent moiety such as but

not limited to at least one of a carbon, oxygen, nitrogen, silicon, aluminum, boron, germanium and tin atom or a combination thereof. Preferably bridging group A* contains a carbon, silicon or germanium atom, most preferably A* contains at least one silicon atom or at least one carbon atom. The bridging group A* may also contain substituent groups R* as defined above including halogens and iron. Non-limiting examples of bridging group A* may be represented by R'₂C, R'₂CCR'₂, R'₂Si, R'₂SiCR'₂, R'₂SiSiR'₂, R'₂Ge, R'P, R'N, R'B where R' is independently, a radical group which is hydride, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-substituted organometalloid, disubstituted boron, disubstituted pnictogen, substituted chalcogen, or halogen or two or more R' may be joined to form a ring or ring system. In one embodiment, the bridged, bulky ligand metallocene catalyst compounds of Formula 2 have two or more bridging groups A* (EP 664 301 B1). In another embodiment, the bulky ligand metallocene catalyst compounds are those where the R* substituents on the bulky ligands L^A and L^B of Formulas 1 and 2 are substituted with the same or different number of substituents on each of the bulky ligands. In another embodiment, the bulky ligands L^A and L^B of Formulas 1 and 2 are different from each other.

[00121] Other bulky ligand metallocene catalyst compounds and catalyst systems useful in the invention may include those described in U.S. Patent Nos. 5,064,802, 5,145,819, 5,149,819, 5,243,001, 5,239,022, 5,276,208, 5,296,434, 5,321,106, 5,329,031, 5,304,614, 5,677,401, 5,723,398, 5,753,578, 5,854,363, 5,856,547 5,858,903, 5,859,158, 5,900,517 and 5,939,503 and PCT publications WO 93/08221, WO 93/08199, WO 95/07140, WO 98/11144, WO 98/41530, WO 98/41529, WO 98/46650, WO 99/02540 and WO 99/14221 and European publications EP-A-0 578 838, EP-A-0 638 595, EP-B-0 513 380, EP-A1-0 816 372, EP-A2-0 839 834, EP-B1-0 632 819, EP-B1-0 748 821 and EP-B1-0 757 996, all of which are herein fully incorporated by reference.

[00122] In another embodiment, the catalyst compositions useful in the invention may include bridged heteroatom, mono-bulky ligand metallocene compounds. These types of catalysts and catalyst systems are described in, for example, PCT publication WO 92/00333, WO 94/07928, WO 91/04257, WO 94/03506, WO96/00244, WO 97/15602 and WO 99/20637 and U.S. Patent Nos. 5,057,475, 5,096,867, 5,055,438, 5,198,401, 5,227,440 and 5,264,405 and European publication EP-A-0 420 436, all of which are herein fully incorporated by reference.

[00123] In another embodiment, the catalyst composition useful in the invention includes one or more bulky ligand metallocene catalyst compounds represented by Formula 3:



where M is a Group 3 to 16 metal atom or a metal selected from the Group of actinides and lanthanides of the Periodic Table of Elements, preferably M is a Group 3 to 12 transition metal, and more preferably M is a Group 4, 5 or 6 transition metal, and most preferably M is a Group 4 transition metal in any oxidation state, and is especially titanium; L^c is a substituted or unsubstituted bulky ligand bonded to M; J* is bonded to M; A* is bonded to J* and L^c; J* is a heteroatom ancillary ligand; and A* is a bridging group; Q* is a univalent anionic ligand; and n is the integer 0, 1 or 2. In Formula 3 above, L^c, A* and J* form a fused ring system. In an embodiment, L^c of Formula 3 is as defined above for L^A. A*, M and Q* of Formula 3 are as defined above in Formula 1. In Formula 3, J* is a heteroatom containing ligand in which J* is an element with a coordination number of three from Group 15 or an element with a coordination number of two from Group 16 of the Periodic Table of Elements. Preferably J* contains a nitrogen, phosphorus, oxygen or sulfur atom with nitrogen being most preferred. In an embodiment of the invention, the bulky ligand metallocene catalyst

compounds are heterocyclic ligand complexes where the bulky ligands, the ring(s) or ring system(s), include one or more heteroatoms or a combination thereof. Non-limiting examples of heteroatoms include a Group 13 to 16 element, preferably nitrogen, boron, sulfur, oxygen, aluminum, silicon, phosphorous and tin. Examples of these bulky ligand metallocene catalyst compounds are described in WO 96/33202, WO 96/34021, WO 97/17379 and WO 98/22486 and EP-A1-0 874 005 and U.S. Patent No. 5,637,660, 5,539,124, 5,554,775, 5,756,611, 5,233,049, 5,744,417, and 5,856,258 all of which are herein incorporated by reference.

[00124] In one embodiment, the bulky ligand metallocene compounds (precatalysts) are those complexes based on bidentate ligands containing pyridine or quinoline moieties, such as those described in U.S. Application Serial No. 09/103,620 filed June 23, 1998, which is herein incorporated by reference. In another embodiment, the bulky ligand metallocene catalyst compounds are those described in PCT publications WO 99/01481 and WO 98/42664, which are fully incorporated herein by reference.

[00125] In another embodiment, the bulky ligand metallocene catalyst compound is a complex of a metal, preferably a transition metal, a bulky ligand, preferably a substituted or unsubstituted pi-bonded ligand, and one or more heteroallyl moieties, such as those described in U.S. Patent Nos. 5,527,752 and 5,747,406 and EP-B1-0 735 057, all of which are herein fully incorporated by reference.

[00126] In another embodiment, the bulky ligand metallocene catalyst compounds are those described in PCT publications WO 99/01481 and WO 98/42664, which are fully incorporated herein by reference.

[00127] Useful Group 6 bulky ligand metallocene catalyst systems are described in U.S. Patent No. 5,942,462, which is incorporated herein by reference.

[00128] Still other useful catalysts include those multinuclear metallocene catalysts as described in WO 99/20665 and 6,010,794, and transition metal metaaracyle structures described in EP 0 969 101 A2, which are herein incorporated herein by reference. Other metallocene catalysts include those described in EP 0 950 667 A1, double cross-linked metallocene catalysts (EP 0 970 074 A1), tethered metallocenes (EP 970 963 A2) and those sulfonyl catalysts described in U.S. Patent No. 6,008,394, which are incorporated herein by reference.

[00129] It is also contemplated that in one embodiment the bulky ligand metallocene catalysts, described above, include their structural or optical or enantiomeric isomers (meso and racemic isomers, for example see U.S. Patent No. 5,852,143, incorporated herein by reference) and mixtures thereof.

[00130] It is further contemplated that any one of the bulky ligand metallocene catalyst compounds, described above, have at least one fluoride or fluorine containing leaving group as described in U.S. Application Serial No. 09/191,916 filed November 13, 1998.

[00131] The Group 15 containing metal compounds utilized in the catalyst composition of the invention are prepared by methods known in the art, such as those disclosed in EP 0 893 454 A1, U.S. Patent No. 5,889,128 and the references cited in U.S. Patent No. 5,889,128 which are all herein incorporated by reference. U.S. Application Serial Number 09/312,878, filed May 17, 1999, discloses a gas or slurry phase polymerization process using a supported bisamide catalyst, which is also incorporated herein by reference.

[00132] For additional information of Group 15 containing metal compounds, please see Mitsui Chemicals, Inc. in EP 0 893 454 A1 which discloses transition metal amides combined with activators to polymerize olefins.

[00133] In one embodiment the Group 15 containing metal compound is allowed to age prior to use as a polymerization. It has been noted on at least one occasion that one such catalyst compound (aged at least 48 hours) performed better than a newly prepared catalyst compound.

[00134] It is further contemplated that bis-amide based pre-catalysts may be used. Exemplary compounds include those described in the patent literature. International patent publications WO 96/23010, WO 97/48735 and Gibson, et al., Chem. Comm., pp. 849-850 (1998), which disclose diimine-based ligands for Group-8-10 compounds that undergo ionic activation and polymerize olefins. Polymerization catalyst systems from Group-5-10 metals, in which the active center is highly oxidized and stabilized by low-coordination-number, polyanionic, ligand systems, are described in U.S. Patent 5,502,124 and its divisional U.S. Patent 5,504,049. See also the Group-5 organometallic catalyst compounds of U.S. Patent 5,851,945 and the tridentate-ligand-containing, Group-5-10, organometallic catalysts of U.S. Patent No. 6, 294, 495. Group-11 catalyst precursor compounds, activatable with ionizing cocatalysts, useful for olefin and vinylic polar molecules are described in WO 99/30822.

[00135] Other useful catalyst compounds are those Group 5 and 6 metal imido complexes described in EP-A2-0 816 384 and U.S. Patent No. 5,851,945, which is incorporated herein by reference. In addition, metallocene catalysts include bridged bis(aryl amido) Group 4 compounds described by D. H. McConville, et al., in Organometallics 1995, 14, 5478-5480, which is herein incorporated by reference. In addition, bridged bis(amido) catalyst compounds are described in WO 96/27439, which is herein incorporated by reference. Other

useful catalysts are described as bis(hydroxy aromatic nitrogen ligands) in U.S. Patent No. 5,852,146, which is incorporated herein by reference. Other useful catalysts containing one or more Group 15 atoms include those described in WO 98/46651, which is herein incorporated herein by reference.

[00136] U.S. Patent 5,318,935 describes bridged and unbridged, bisamido catalyst compounds of Group-4 metals capable of alpha-olefins polymerization. Bridged bi(arylarnido)-Group-4 compounds for olefin polymerization are described by D. H. McConville, et al., in *Organometallics* 1995, 14, 5478-5480. This reference presents synthetic methods and compound characterizations. Further work appearing in D. H. McConville, et al, *Macromolecules* 1996, 29, 5241-5243, describes bridged bis(arylarnido)-Group-4 compounds that are polymerization catalysts for 1-hexene. Additional invention-suitable transition metal compounds include those described in WO 96/40805. Cationic Group-3- or Lanthanide-metal olefin polymerization complexes are disclosed in copending U.S. Application Ser. No. 09/408,050, filed 29 September 1999. A monoanionic bidentate ligand and two monoanionic ligands stabilize those catalyst precursors, which can be activated with this invention's ionic cocatalysts.

[00137] The literature describes many additional suitable catalyst-precursor compounds. Compounds that contain abstractable ligands or that can be alkylated to contain abstractable ligands suit this invention. See, for instance, V. C. Gibson, et al; "The Search for New-Generation Olefin Polymerization Catalysts: Life Beyond Metallocenes", *Angew. Chem. Int. Ed.*, 38, 428-447 (1999).

[00138] This invention may also be practiced with the catalysts containing phenoxide ligands such as those disclosed in EP 0 874 005 A1, which is incorporated by reference herein.

[00139] In another embodiment, conventional-type transition metal catalysts may be used in the practice of this invention. Conventional-type transition metal catalysts are those traditional Ziegler-Natta, vanadium and Phillips-type catalysts well known in the art. Such as, for example Ziegler-Natta catalysts as described in Ziegler-Natta Catalysts and Polymerizations, John Boor, Academic Press, New York, 1979. Examples of conventional-type transition metal catalysts are also discussed in U.S. Patent Nos. 4,115,639, 4,077,904, 4,482,687, 4,564,605, 4,721,763, 4,879,359 and 4,960,741, all of which are herein fully incorporated by reference. The conventional-type transition metal catalyst compounds that may be used in the present invention include transition metal compounds from Groups 3 to 17, preferably 4 to 12, more preferably 4 to 6 of the Periodic Table of Elements.

[00140] Preferred conventional-type transition metal catalysts may be represented by the formula: MR_x , where M is a metal from Groups 3 to 17, preferably Group 4 to 6, more preferably Group 4, most preferably titanium; R is a halogen or a hydrocarbyloxy group; and x is the oxidation state of the metal M. Non-limiting examples of R include alkoxy, phenoxy, bromide, chloride and fluoride. Non-limiting examples of conventional-type transition metal catalysts where M is titanium include $TiCl_4$, $TiBr_4$, $Ti(OC_2H_5)_3Cl$, $Ti(OC_2H_5)Cl_3$, $Ti(OC_4H_9)_3Cl$, $Ti(OC_3H_7)_2Cl_2$, $Ti(OC_2H_5)_2Br_2$, $TiCl_3 \bullet 1/3 AlCl_3$ and $Ti(OC_{12}H_{25})Cl_3$.

[00141] Conventional-type transition metal catalyst compounds based on magnesium/titanium electron-donor complexes that are useful in the invention are described in, for example, U.S. Patent Nos. 4,302,565 and 4,302,566, which are herein fully incorporate by reference. The $MgTiCl_6$ (ethyl acetate)₄ derivative is particularly preferred.

[00142] British Patent Application 2,105,355 and U.S. Patent No. 5,317,036, herein incorporated by reference, describes various conventional-type vanadium catalyst compounds. Non-limiting examples of conventional-type

vanadium catalyst compounds include vanadyl trihalide, alkoxy halides and alkoxides such as VOCl_3 , $\text{VOCl}_2(\text{OBu})$ where Bu =butyl and $\text{VO}(\text{OC}_2\text{H}_5)_3$; vanadium tetra-halide and vanadium alkoxy halides such as VCl_4 and $\text{VCl}_3(\text{OBu})$; vanadium and vanadyl acetyl acetonates and chloroacetyl acetonates such as $\text{V}(\text{AcAc})_3$ and $\text{VOCl}_2(\text{AcAc})$ where (AcAc) is an acetyl acetonate. The preferred conventional-type vanadium catalyst compounds are VOCl_3 , VCl_4 and $\text{VOCl}_2\text{-OR}$ where R is a hydrocarbon radical, preferably a C₁ to C₁₀ aliphatic or aromatic hydrocarbon radical such as ethyl, phenyl, isopropyl, butyl, propyl, n-butyl, iso-butyl, tertiary-butyl, hexyl, cyclohexyl, naphthyl, etc., and vanadium acetyl acetonates.

[00143] Conventional-type chromium catalyst compounds, often referred to as Phillips-type catalysts, suitable for use in the present invention include CrO_3 , chromocene, silyl chromate, chromyl chloride (CrO_2Cl_2), chromium-2-ethyl-hexanoate, chromium acetylacetone ($\text{Cr}(\text{AcAc})_3$), and the like. Non-limiting examples are disclosed in U.S. Patent Nos. 3,709,853, 3,709,954, 3,231,550, 3,242,099 and 4,077,904, which are herein fully incorporated by reference.

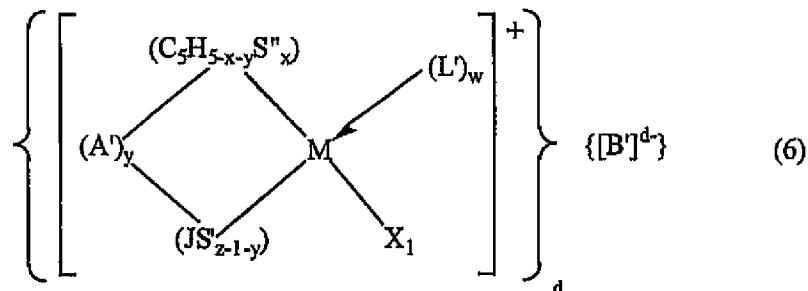
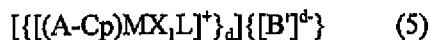
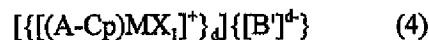
[00144] Still other conventional-type transition metal catalyst compounds and catalyst systems suitable for use in the present invention are disclosed in U.S. Patent Nos. 4,124,532, 4,302,565, 4,302,566, 4,376,062, 4,379,758, 5,066,737, 5,763,723, 5,849,655, 5,852,144, 5,854,164 and 5,869,585 and published EP-A2 0 416 815 A2 and EP-A1 0 420 436, which are all herein incorporated by reference.

[00145] Other catalysts may include cationic catalysts such as AlCl_3 , and other cobalt, iron, nickel and palladium catalysts well known in the art. See for example U.S. Patent Nos. 3,487,112, 4,472,559, 4,182,814 and 4,689,437, all of which are incorporated herein by reference.

[00146] It is also contemplated that other catalysts can be combined with the catalyst compounds in the catalyst composition useful in the invention. For example, see U.S. Patent Nos. 4,937,299, 4,935,474, 5,281,679, 5,359,015, 5,470,811, and 5,719,241 all of which are herein fully incorporated herein by reference.

[00147] It is further contemplated that one or more of the catalyst compounds described above or catalyst systems may be used in combination with one or more conventional catalyst compounds or catalyst systems. Non-limiting examples of mixed catalysts and catalyst systems are described in U.S. Patent Nos. 4,159,965, 4,325,837, 4,701,432, 5,124,418, 5,077,255, 5,183,867, 5,391,660, 5,395,810, 5,691,264, 5,723,399 and 5,767,031 and PCT Publication WO 96/23010 published August 1, 1996, all of which are herein fully incorporated by reference.

[00148] Preferred metallocene catalysts used in this invention can more specifically be represented by one of the following general formulae (all references to Groups being the new Group notation of the Period Table of the Elements as described by Chemical and Engineering News, 63(5), 27, 1985):



wherein:

(A-Cp) is either (Cp), (Cp*) or Cp-A'-Cp*; Cp and Cp* are the same or different cyclopentadienyl rings substituted with from zero to five substituent groups S'', each substituent group S'' being, independently, a radical group which is a hydrocarbyl, substituted-hydrocarbyl, halocarbyl, substituted-halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-substituted organometalloid, disubstituted boron, disubstituted pnictogen, substituted chalcogen or halogen radicals, or Cp and Cp* are cyclopentadienyl rings in which any two adjacent S'' groups are joined forming a C₄ to C₂₀ ring to give a saturated or unsaturated polycyclic cyclopentadienyl ligand; Cp and Cp* may also have one or two carbon atoms within the ring replaced by a Group 15 or 16 element especially, S, O, N or P;

A' is a bridging group;

(C_sH_{5-y-x}S''_x) is a cyclopentadienyl ring substituted with from zero to five S'' radicals as defined above;

x is from 0 to 5 denoting the degree of substitution;

M is titanium, zirconium or hafnium;

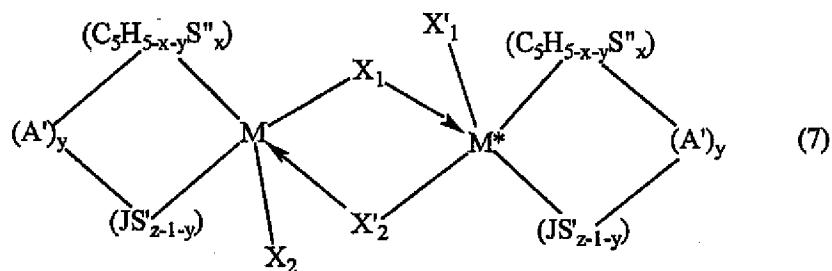
X₁ is a hydride radical, hydrocarbyl radical, substituted- hydrocarbyl radical, hydrocarbyl-substituted organometalloid radical or halocarbyl-substituted organometalloid radical which radical may optionally be covalently bonded to both or either M and L or L' or all or any M, S'' or S', and provided that X₁ is not a substituted or unsubstituted cyclopentadienyl ring;

(JS'_{z-1-y}) is a heteroatom ligand in which J is an element from Group 15 of the Periodic Table of Elements with a coordination number of 3 or an element from Group 16 with a coordination number of 2; S' is a radical group which is a

hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, hydrocarbyl-substituted organometalloid, or halocarbyl-substituted organometalloid; and z is the coordination number of the element J;

y is 0 or 1;

L is an olefin, diolefin or aryne ligand. L' is the same as L, and can additionally be an amine, phosphine, ether, or sulfide ligand, or any other neutral Lewis base; L' can also be a second transition metal compound of the same type such that the two metal center M and M* are bridged by X₁ and X'₁, wherein M* has the same meaning as M, X'₁, X₂ and X'₂ have the same meaning as X₁, where such dimeric compounds which are precursors to the cationic portion of the catalyst are represented by the formula:



wherein

w is an integer from 0 to 3;

B' is a chemically stable, non-nucleophilic anionic complex having a molecular diameter about or greater than 4 Angstroms or an anionic Lewis-acid activator resulting from the reaction of a Lewis-acid activator with the precursor to the cationic portion of the catalyst system described in formulae 1-4. When B' is a Lewis-acid activator, X₁ can also be an alkyl group donated by the Lewis-acid activator; and

d is an integer representing the charge of B'.

[00149] The catalysts are preferably prepared by combining at least two components. In one preferred method, the first component is a cyclopentadienyl derivative of a Group 4 metal compound containing at least one ligand which will combine with the second component or at least a portion thereof such as a cation portion thereof. The second component is an ion-exchange compound comprising a cation which will irreversibly react with at least one ligand contained in said Group 4 metal compound (first component) and a non-coordinating anion which is either a single coordination complex comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central formally charge-bearing metal or metalloid atom or an anion comprising a plurality of boron atoms such as polyhedral boranes, carboranes and metallacarboranes.

[00150] In general, suitable anions for the second component may be any stable and bulky anionic complex having the following molecular attributes: 1) the anion should have a molecular diameter greater than 4 Angstroms; 2) the anion should form stable ammonium salts; 3) the negative charge on the anion should be delocalized over the framework of the anion or be localized within the core of the anion; 4) the anion should be a relatively poor nucleophile; and 5) the anion should not be a powerful reducing or oxidizing agent. Anions meeting these criteria-- such as polynuclear boranes, carboranes, metallacarboranes, polyoxoanions and anionic coordination complexes are well described in the chemical literature.

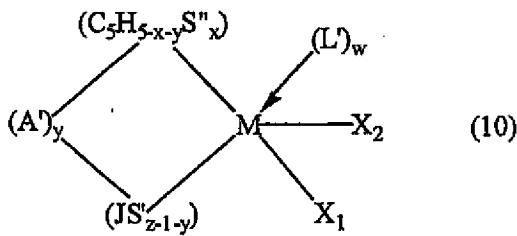
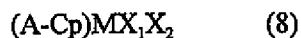
[00151] The cation portion of the second component may comprise Bronsted acids such as protons or protonated Lewis bases or may comprise Lewis acids such as ferricinium, tropylium, triphenylcarbenium or silver cations.

[00152] In another preferred method, the second component is a Lewis-acid complex which will react with at least one ligand of the first component, thereby forming an ionic species described in formulae 4-6 with the ligand abstracted from the first component now bound to the second component. Alumoxanes and especially methylalumoxane, the product formed from the reaction of trimethylaluminum in an aliphatic or aromatic hydrocarbon with stoichiometric quantities of water, are particularly preferred Lewis-acid second components. Modified alumoxanes are also preferred. Alumoxanes are well known in the art and methods for their preparation are illustrated by U.S. Pat. Nos. 4,542,199; 4,544,762; 5,015,749; and 5,041,585. A technique for preparing modified alumoxanes has been disclosed in U.S. Pat. No. 5,041,584, in EPA 0 516 476, and in EPA 0 561 476, which are incorporated by reference herein.

[00153] Upon combination of the first and second components, the second component reacts with one of the ligands of the first component, thereby generating an anion pair consisting of a Group 4 metal cation and the aforementioned anion, which anion is compatible with and non-coordinating towards the Group 4 metal cation formed from the first component. The anion of the second compound must be capable of stabilizing the Group 4 metal cation's ability to function as a catalyst and must be sufficiently labile to permit displacement by an olefin, diolefin or an acetylenically unsaturated monomer during polymerization. The catalysts of this invention may be supported. U.S. Pat. Nos. 4,808,561, issued Feb. 28, 1989; 4,897,455 issued Jan. 3, 1990; 5,057,475 issued Oct. 15, 1991; U.S. patent application Ser. No. 459,921 (published as PCT International publication WO 91/09882), Canadian Patent 1,268,753, U.S. Pat. No. 5,240,894 and WO 94 03506 disclose such supported catalysts and the methods to produce such and are herein incorporated by reference.

[00154] The Group 4 metal compounds; i.e., titanium, zirconium and hafnium metallocene compounds, useful as first compounds (pre-catalysts) in the

preparation of the preferred metallocene catalysts of this invention are cyclopentadienyl derivatives of titanium, zirconium and hafnium. In general, useful titanocenes, zirconocenes and hafnocenes may be represented by the following general formulae:



wherein:

$(A\text{-Cp})$ is either $(\text{Cp})(\text{Cp}^*)$ or $\text{Cp}\text{-A}'\text{-Cp}^*$; Cp and Cp^* are the same or different cyclopentadienyl rings substituted with from zero to five substituent groups S'' , each substituent group S'' being, independently, a radical group which is a hydrocarbyl, substituted-hydrocarbyl, halocarbyl, substituted-halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-substituted organometalloid, disubstituted boron, disubstituted pnictogen, substituted chalcogen or halogen radicals, or Cp and Cp^* are cyclopentadienyl rings in which any two adjacent S'' groups are joined forming a C_4 to C_{20} ring to give a saturated or unsaturated polycyclic cyclopentadienyl ligand;

A' is a bridging group;

y is 0 or 1;

$(\text{C}_5\text{H}_{5-\text{y}-\text{x}}\text{S}''_{\text{x}})$ is a cyclopentadienyl ring substituted with from zero to five S'' radicals as defined above;

x is from 0 to 5 denoting the degree of substitution;

(JS'_{z-1-y}) is a heteroatom ligand in which J is an element from Group 15 of the Periodic Table of Elements with a coordination number of 3 or an element from Group 16 with a coordination number of 2, S' is a radical group which is a hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, hydrocarbyl-substituted organometalloid, or halocarbyl-substituted organometalloid; and z is the coordination number of the element J;

L is an olefin, diolefin or aryne ligand. L' is the same as L and can additionally be an amine, phosphine, ether, or sulfide ligand, or any other neutral Lewis base; L' can also be a second transition metal compound of the same type such that the two metal centers M and M* are bridged by X₁ and X'₁, wherein M* has the same meaning as M, X'₁ has the same meaning as X₁ and X'₂ has the same meaning as X₂ where such dimeric compounds which are precursors to the cationic portion of the catalyst are represented by formula 7 above;

w is an integer from 0 to 3; and

X₁ and X₂ are, independently, hydride radicals, hydrocarbyl radicals, substituted hydrocarbyl radicals, halocarbyl radicals, substituted halocarbyl radicals, and hydrocarbyl- and halocarbyl-substituted organometalloid radicals, substituted pnictogen radicals, or substituted chalcogen radicals; or X₁ and X₂ are joined and bound to the metal atom to form a metallacycle ring containing from about 3 to about 20 carbon atoms; or X₁ and X₂ together can be an olefin, diolefin or aryne ligand; or when Lewis-acid activators, such as methylalumoxane, which are capable of donating an X₁ ligand as described above to the transition metal component are used, X₁ and X₂ may independently be a halogen, alkoxide, aryloxide, amide, phosphide or other univalent anionic ligand or both X₁ and X₂

can also be joined to form a anionic chelating ligand and with the proviso that X_1 and X_2 are not a substituted or unsubstituted cyclopentadienyl ring.

[00155] Table A depicts representative constituent moieties for the metallocene components of formulae 7-10. The list is for illustrative purposes only and should not be construed to be limiting in any way. A number of final components may be formed by permuting all possible combinations of the constituent moieties with each other. When hydrocarbyl radicals including alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, cycloalkynyl and aromatic radicals are disclosed in this application the term includes all isomers. For example, butyl includes n-butyl, 2-methylpropyl, 1-methylpropyl, tert-butyl, and cyclobutyl; pentyl includes n-pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 1-ethylpropyl, neopentyl, cyclopentyl and methylcyclobutyl; butenyl includes E and Z forms of 1-butenyl, 2-butenyl, 3-butenyl, 1-methyl-1-propenyl, 1-methyl-2-propenyl, 2-methyl-1-propenyl and 2-methyl-2-propenyl. This includes when a radical is bonded to another group, for example, propylcyclopentadienyl include n-propylcyclopentadienyl, isopropylcyclopentadienyl and cyclopropylcyclopentadienyl. In general, the ligands or groups illustrated in Table A include all isomeric forms. For example, dimethylcyclopentadienyl includes 1,2-dimethylcyclopentadienyl and 1,3-dimethylcyclopentadienyl; methylindenyl includes 1-methylindenyl, 2-methylindenyl, 3-methylindenyl, 4-methylindenyl, 5-methylindenyl, 6-methylindenyl and 7-methylindenyl; methylethylphenyl includes ortho-methylethylphenyl, meta-methylethylphenyl and para-methylethylphenyl. Examples of specific invention catalyst precursors take the following formula where some components are listed in Table A. To illustrate members of the transition metal component, select any combination of the species listed in Tables A. For nomenclature purposes, for the bridging group, A', the words "silyl" and "silylene" are used interchangeably, and represent a diradical species. For the bridging group A', "ethylene" refers to a 1,2-ethylene linkage and is distinguished from ethene-1,1-diyl. Thus, for the bridging group A', "ethylene" and "1,2-

"ethylene" are used interchangeably. For compounds possessing a bridging group, A', the bridge position on the cyclopentadienyl-type ring is always considered the 1-position. Thus, for example, the use of "1-fluorenyl" is interchangeable with the use of "fluorenyl"

[00156] Illustrative compounds of the formula 8 type are:

bis(cyclopentadienyl)hafnium dimethyl, ethylenebis(tetrahydroindenyl)zirconium dihydride, bis(pentamethyl)zirconium diethyl, dimethylsilyl(1-fluorenyl)(cyclopentadienyl)titanium dichloride and the like. Illustrative compounds of the formula 9 type are: bis(cyclopentadienyl)(1,3-butadiene)zirconium, bis(cyclopentadienyl)(2,3-dimethyl-1,3-butadiene)zirconium, bis(pentamethylcyclopentadienyl)(benzene)zirconium, bis(pentamethylcyclopentadienyl)titanium ethylene and the like. Illustrative compounds of the formula 10 type are:
dimethylsilyl(tetramethylcyclopentadienyl)(t-butylamido)zirconium dichloride, ethylene(methylcyclopentadienyl)(phenylamido)titanium dimethyl, methylphenylsilyl(indenyl)(phenyphosphido)hafnium dihydride and (pentamethylcyclopentadienyl)(di-t-butylamido)hafnium dimethoxide.

[00157] The conditions under which complexes containing neutral Lewis base ligands such as ether or those which form dimeric compounds is determined by the steric bulk of the ligands about the metal center. For example, the t-butyl group in $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N-t-Bu})\text{ZrCl}_2$ has greater steric requirements than the phenyl in $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{NPh})\text{ZrCl}_2 \cdot \text{Et}_2\text{O}$ thereby not permitting ether coordination in the former compound in its solid state. Similarly, due to the decreased steric bulk of the trimethylsilylcyclopentadienyl group in $[\text{Me}_2\text{Si}(\text{Me}_3\text{SiC}_5\text{H}_3)(\text{N-t-Bu})\text{ZrCl}_2]_2$ versus that of the tetramethylcyclopentadienyl group in $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N-t-Bu})\text{ZrCl}_2$, the former compound is dimeric and the latter is not.

TABLE A

<u>A'</u>	Cp, Cp*, CpR or (C ₃ H _{5-y,x} S")
Dimethylsilylene	Cyclopentadienyl
Diethylsilylene	Methylcyclopentadienyl
dipropylsilylene	Dimethylcyclopentadienyl
dibutylsilylene	Trimethylcyclopentadienyl
dipentylsilylene	Tetramethylcyclopentadienyl
dihexylsilylene	Pentamethylcyclopentadienyl (no A')
diheptylsilylene	Ethylcyclopentadienyl
dioctylsilylene	Diethylcyclopentadienyl
dinonylsilylene	Propylcyclopentadienyl
didecylsilylene	Dipropylcyclopentadienyl
diundecylsilylene	Butylcyclopentadienyl
didodecylsilylene	Dibutylcyclopentadienyl
ditridecylsilylene	Pentylcyclopentadienyl
ditetradecylsilylene	Dipentylcyclopentadienyl
dipentadecylsilylene	Hexylcyclopentadienyl
dihexadecylsilylene	Dihexylcyclopentadienyl
diheptadecylsilylene	Heptylcyclopentadienyl
dioctadecylsilylene	Diheptylcyclopentadienyl
dinonadecylsilylene	Octylcyclopentadienyl
dieicosylsilylene	Dioctylcyclopentadienyl
diheneicosylsilylene	nonylcyclopentadienyl
didocosylsilylene	dinonylcyclopentadienyl
ditricosylsilylene	decylcyclopentadienyl
ditetracosylsilylene	didecylcyclopentadienyl
dipentacosylsilylene	undecylcyclopentadienyl
dihexacosylsilylene	dodecylcyclopentadienyl
diheptacosylsilylene	tridecylcyclopentadienyl
dioctacosylsilylene	tetradecylcyclopentadienyl
dinonacosylsilylene	pentadecylcyclopentadienyl (no A')
ditriacontylsilylene	hexadecylcyclopentadienyl
dicyclohexylsilylene	heptadecylcyclopentadienyl
dicyclopentylsilylene	octadecylcyclopentadienyl
dicycloheptylsilylene	nonadecylcyclopentadienyl
dicyclooctylsilylene	eicosylcyclopentadienyl
dicyclodecylsilylene	heneicosylcyclopentadienyl
dicyclododecylsilylene	docosylcyclopentadienyl
dinaphylsilylene	tricosylcyclopentadienyl

diphenylsilylene	tetracosylcyclopentadienyl
ditolylsilylene	pentacosylcyclopentadienyl
dibenzylsilylene	hexacosylcyclopentadienyl
diphenethylsilylene	heptacosylcyclopentadienyl
di(butylphenethyl)silylene	octacosylcyclopentadienyl
methylethylsilylene	nonacosylcyclopentadienyl
methylpropylsilylene	triacontylcyclopentadienyl
methylbutylsilylene	cyclohexylcyclopentadienyl
methylhexylsilylene	phenylcyclopentadienyl
methylphenylsilylene	diphenylcyclopentadienyl
ethylphenylsilylene	triphenylcyclopentadienyl
ethylpropylsilylene	tetraphenylcyclopentadienyl
ethylbutylsilylene	pentaphenylcyclopentadienyl
propylphenylsilylene	tolylcyclopentadienyl
dimethylgermylene	benzylcyclopentadienyl
diethylgermylene	phenethylcyclopentadienyl
diphenylgermylene	cyclohexylmethylcyclopentadienyl
methylphenylgermylene	naphylcyclopentadienyl
Cyclotetramethylenesilylen	methylphenylcyclopentadienyl
Cyclopentamethylenesilyle	methyltolylcyclopentadienyl
cyclotrimethylenesilylene	methyllethylcyclopentadienyl
cyclohexylazanediy	methylpropylcyclopentadienyl
butylazanediy	methylbutylcyclopentadienyl
methylazanediy	methylpentylcyclopentadienyl
phenylazanediy	methylhexylcyclopentadienyl
perfluorophenylazanediy	methylheptylcyclopentadienyl
methylphosphanediy	methyloctylcyclopentadienyl
ethylphosphanediy	methylnonylcyclopentadienyl
propylphosphanediy	methyldecylcyclopentadienyl
butylphosphanediy	vinylcyclopentadienyl
cyclohexylphosphanediy	propenylcyclopentadienyl
phenylphosphanediy	butenylcyclopentadienyl
methylboranediy	indenyl
phenylboranediy	methylindenyl
methylene	dimethylindenyl
dimethylmethylen	trimethylindenyl
diethylmethylen	methylpropylindenyl
dibutylmethylen	dimethylpropylindenyl
dipropylmethylen	methyl dipropylindenyl

diphenylmethylene	methylethylindenyl
ditolylmethylene	methylbutylindenyl
di(butylphenyl)methylene	ethylindenyl
di(trimethylsilylphenyl)met	propylindenyl
di(triethylsilylphenyl)meth	butylindenyl
dibenzylmethlene	pentylindenyl
Cyclotetramethylenemethyl	hexylindenyl
Cyclopentamethylenemeth	heptylindenyl
ethylene	octylindenyl
methylethylene	nonylindenyl
dimethylethylene	decylindenyl
trimethylethylene	phenylindenyl
tetramethylethylene	(fluorophenyl)indenyl
cyclopentylene	(methylphenyl)indenyl
cyclohexylene	biphenylindenyl
cycloheptylene	(bis(trifluoromethyl)phenyl)indenyl
cyclooctylene	naphylindenyl
propanediyl	phenanthrylindenyl
methylpropanediyl	benzylindenyl
dimethylpropanediyl	benzindenyl
trimethylpropanediyl	cyclohexylindenyl
tetramethylpropanediyl	methylphenylindenyl
pentamethylpropanediyl	ethylphenylindenyl
hexamethylpropanediyl	propylphenylindenyl
tetramethyldisiloxylene	methylnapthylindenyl
vinylene	ethylnapthylindenyl
ethene-1,1-diyl	propynapthylindenyl
divinylsilylene	(methylphenyl)indenyl
dipropenylsilylene	(dimethylphenyl)indenyl
dibutenylsilylene	(ethylphenyl)indenyl
methylvinylsilylene	(diethylphenyl)indenyl
methylpropenylsilylene	(propylphenyl)indenyl
methylbutenylsilylene	(dipropylphenyl)indenyl
dimethylsilylmethylene	methyltetrahydroindenyl
diphenylsilylmethylene	dimethyltetrahydroindenyl
dimethylsilylethylene	dimethyldihydroindenyl
diphenylsilylethylene	dimethyltrihydroindenyl
dimethylsilylpropylene	methylphenyltetrahydroindenyl
diphenylsilylpropylene	methylphenyldihydroindenyl

dimethylstannylene	methylphenyltrihydroindenyl
diphenylstannylene	ethyltetrahydroindenyl
	propyltetrahydroindenyl
	butyltetrahydroindenyl
	phenyltetrahydroindenyl
	fluorenyl
	methylfluorenyl
	dimethylfluorenyl
	trimethylfluorenyl
	ethylfluorenyl
	propylfluorenyl
	butylfluorenyl
	dibutylfluorenyl
	pentylfluorenyl
	hexylfluorenyl
	heptylfluorenyl
	octylfluorenyl
	nonylfluorenyl
	decylfluorenyl
	phenylfluorenyl
	napthylfluorenyl
	benzylfluorenyl
	methylphenylfluorenyl
	ethylphenylfluorenyl
	propylphenylfluorenyl
	methylnaphthylfluorenyl
	ethylnaphthylfluorenyl
	propynaphthylfluorenyl
	octahydrofluorenyl
	tetrahydrofluorenyl
	octamethyloctahydrodibenzo[b,h]fluorenyl
	tetramethyltetrahydrobenzo[b]fluorenyl
	diphenylmethylcyclopentadienyl
	trimethylsilylcyclopentadienyl
	triethylsilylcyclopentadienyl
	trimethylgermylcyclopentadienyl
	trimethylstannylcyclopentadienyl
	triethylplumbylcyclopentadienyl
	trifluoromethylcyclopentadienyl

	N,N-dimethylamidocyclopentadienyl
	P,P-dimethylphosphidocyclopentadienyl
	N,N-diethylamidocyclopentadienyl
	methoxycyclopentadienyl
	ethoxycyclopentadienyl
	trimethylsiloxy cyclopentadienyl
	(N,N-dimethylamido methyl)cyclopentadienyl
	methoxyindenyl
	dimethoxyindenyl
	N,N-dimethylaminoindenyl
	trimethylsiloxyindenyl
	butyldimethylsiloxyindenyl
	bis(N,N-dimethylamino)indenyl
	di(trimethylsiloxy)indenyl
	di(butyldimethylsiloxy)indenyl
	methoxyfluorenyl
	dimethoxyfluorenyl
	N,N-dimethylaminofluorenyl
	trimethylsiloxyfluorenyl
	butyldimethylsiloxyfluorenyl
	dimethoxyfluorenyl
	bis(N,N-dimethylamino)fluorenyl
	di(trimethylsiloxy)fluorenyl
	di(butyldimethylsiloxy)fluorenyl

Table A (continued)

(JS' _{z-l,y}) (y = 1)	X ₁ or X ₂	M
methylamido	chloride	titanium
ethylamido	bromide	zirconium
propylamido	iodide	hafnium
butylamido	fluoride	
pentylamido	hydride	L or L' (optional)
hexylamido	methyl	ethylene
heptylamido	ethyl	propylene
octylamido	propyl	butene
nonylamido	butyl	hexene
decylamido	pentyl	styrene
eicosylamido	hexyl	hexadiene

heneicosylamido	heptyl	butadiene
docosylamido	octyl	dimethylbutadiene
tricosylamido	nonyl	pentadiene
tetracosylamido	decyl	methylhexadiene
pentacosylamido	undecyl	dimethylhexadiene
hexacosylamido	dodecyl	acetylene
heptacosylamido	tridecyl	methylacetylene
octacosylamido	tetradecyl	ethylacetylene
nonacosylamido	pentadecyl	benzyne
triacontylamido	hexadecyl	cyclopentene
phenylamido	heptadecyl	cyclohexene
tolylamido	octadecyl	
phenethylamido	nonadecyl	<u>L' (optional)</u>
benzylamido	eicosyl	diethylether
cyclobutylamido	heneicosyl	dimethylether
cyclopentylamido	docosyl	trimethylamine
cyclohexylamido	tricosyl	triphenylamine
cycloheptylamido	tetracosyl	triethylamine
cyclooctylamido	pentacosyl	tricyclohexylphosphine
cyclononylamido	hexacosyl	triphenylphosphine
cyclododecylamido	heptacosyl	trimethylphosphine
cyclododecylamido	octacosyl	tetrahydrofuran
adamantylamido	nonacosyl	furan
norbornylamido	triacontyl	thiophene
perfluorophenylamido	phenyl	dimethylsulfide
fluorophenylamido	benzyl	diphenylsulfide
difluorophenylamido	phenethyl	
oxo	tolyl	
sulfido	methoxy	
	ethoxy	
(JS' _{z-1-y}) (y = 0)	propoxy	
methoxide	butoxy	
ethoxide	dimethylamido	
phenoxyde	diethylamido	
dimethylphenoxyde	methylmethylethylamido	
dipropylphenoxyde	phenoxy	
methylthio	benzoxy	
ethylthio	allyl	
phenylthio		

dimethylphenylthio		
dipropylphenylthio		
	X ₁ and X ₂ together	
	methylidene	
	ethylidene	
	propylidene	
	tetramethylene	
	pentamethylene	
	hexamethylene	
	ethylenedihydroxy	
	butadiene	
	methylbutadiene	
	dimethylbutadiene	
	pentadiene	
	methylpentadiene	
	dimethylpentadiene	
	hexadiene	
	methylhexadiene	
	dimethylhexadiene	

[00158] Additional preferred catalysts include those described in WO 01/48034, which is incorporated herein by reference. Particularly preferred catalyst compounds include those disclosed at page 9, line 38 to page 25, line 42, page 28, lines 5 to 17, and page 30, line 37 to page 35, line 28.

Activators and Activation Methods for Catalyst Compounds

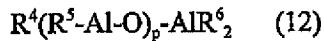
[00159] The polymerization pre-catalyst compounds, described above, are typically activated in various ways to yield compounds having a vacant coordination site that will coordinate, insert, and polymerize olefin(s). For the purposes of this patent specification and appended claims, the terms "cocatalyst" and "activator" are used herein interchangeably and are defined to be any compound which can activate any one of the catalyst compounds described above by converting the neutral catalyst compound to a catalytically active catalyst compound cation. Non-limiting activators, for example, include alumoxanes,

aluminum alkyls, ionizing activators, which may be neutral or ionic, and conventional-type cocatalysts. Preferred activators typically include alumoxane compounds, modified alumoxane compounds, and ionizing anion precursor compounds that abstract one reactive, σ -bound, metal ligand making the metal complex cationic and providing a charge-balancing noncoordinating or weakly coordinating anion.

Aluminoxane and Aluminum Alkyl Activators

[00160] In one embodiment, alumoxane activators are utilized as an activator in the catalyst composition useful in the invention. Alumoxanes are generally oligomeric compounds containing $-Al(R^1)-O-$ sub-units, where R^1 is an alkyl group. Examples of alumoxanes include methylalumoxane (MAO), modified methylalumoxane (MMAO), ethylalumoxane and isobutylalumoxane. Alkylalumoxanes and modified alkylalumoxanes are suitable as catalyst activators, particularly when the abstractable ligand is a halide, alkoxide or amide. Mixtures of different alumoxanes and modified alumoxanes may also be used.

[00161] The activator compounds comprising Lewis-acid activators and in particular alumoxanes are represented by the following general formulae:



[00162] An alumoxane is generally a mixture of both the linear and cyclic compounds. In the general alumoxane formula, R^3 , R^4 , R^5 and R^6 are, independently a $C_1 - C_{30}$ alkyl radical, for example, methyl, ethyl, propyl, butyl,

pentyl, hexyl, heptyl, octyl, nonyl, decyl, and "p" is an integer from 1 to about 50. Most preferably, R³, R⁴, R⁵ and R⁶ are each methyl and "p" is at least 4. When an alkyl aluminum halide or alkoxide is employed in the preparation of the alumoxane, one or more R³⁻⁶ groups may be halide or alkoxide. M' is a metal or metalloid, and Q' is a partially or fully fluorinated hydrocarbyl.

[00163] It is recognized that alumoxane is not a discrete material. A typical alumoxane will contain free trisubstituted or trialkyl aluminum, bound trisubstituted or trialkyl aluminum, and alumoxane molecules of varying degree of oligomerization. Those methylalumoxanes most preferred contain lower levels of trimethylaluminum. Lower levels of trimethylaluminum can be achieved by reaction of the trimethylaluminum with a Lewis base or by vacuum distillation of the trimethylaluminum or by any other means known in the art. It is also recognized that after reaction with the transition metal compound, some alumoxane molecules are in the anionic form as represented by the anion in equations 4-6, thus for our purposes are considered "non-coordinating" anions.

[00164] For further descriptions, see U.S. Patents 4,665,208, 4,952,540, 5,041,584, 5,091,352, 5,206,199, 5,204,419, 4,874,734, 4,924,018, 4,908,463, 4,968,827, 5,329,032, 5,248,801, 5,235,081, 5,157,137, 5,103,031 and EP 0 561 476 A1, EP 0 279 586 B1, EP 0 516 476 A, EP 0 594 218 A1 and WO 94/10180.

[00165] When the activator is an alumoxane (modified or unmodified), some embodiments select the maximum amount of activator at a 5000-fold molar excess Al/M over the catalyst precursor (per metal catalytic site). The minimum activator-to-catalyst-precursor is a 1:1 molar ratio.

[00166] Alumoxanes may be produced by the hydrolysis of the respective trialkylaluminum compound. MMAO may be produced by the hydrolysis of trimethylaluminum and a higher trialkylaluminum such as triisobutylaluminum. MMAO's are generally more soluble in aliphatic solvents and more stable during

storage. There are a variety of methods for preparing alumoxane and modified alumoxanes, non-limiting examples of which are described in U.S. Patent No. 4,665,208, 4,952,540, 5,091,352, 5,206,199, 5,204,419, 4,874,734, 4,924,018, 4,908,463, 4,968,827, 5,308,815, 5,329,032, 5,248,801, 5,235,081, 5,157,137, 5,103,031, 5,391,793, 5,391,529, 5,693,838, 5,731,253, 5,731,451, 5,744,656, 5,847,177, 5,854,166, 5,856,256 and 5,939,346 and European publications EP-A-0 561 476, EP-B1-0 279 586, EP-A-0 594-218 and EP-B1-0 586 665, and PCT publications WO 94/10180 and WO 99/15534, all of which are herein fully incorporated by reference. It may be preferable to use a visually clear methylalumoxane. A cloudy or gelled alumoxane can be filtered to produce a clear solution or clear alumoxane can be decanted from the cloudy solution. Another alumoxane is a modified methyl alumoxane (MMAO) cocatalyst type 3A (commercially available from Akzo Chemicals, Inc. under the trade name Modified Methylalumoxane type 3A, covered under patent number US 5,041,584).

[00167] Aluminum alkyl or organoaluminum compounds which may be utilized as activators (or scavengers) include trimethylaluminum, triethylaluminum, triisobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum and the like.

Ionizing Activators

[00168] It is within the scope of this invention to use an ionizing or stoichiometric activator, neutral or ionic, such as tri (n-butyl) ammonium tetrakis (pentafluorophenyl) boron, a trisperfluorophenyl boron metalloid precursor or a trisperfluoronaphthyl boron metalloid precursor, polyhalogenated heteroborane anions (WO 98/43983), boric acid (U.S. Patent No. 5,942,459) or combination thereof. It is also within the scope of this invention to use neutral or ionic activators alone or in combination with alumoxane or modified alumoxane activators.

[00169] Examples of neutral stoichiometric activators include tri-substituted boron, tellurium, aluminum, gallium and indium or mixtures thereof. The three substituent groups are each independently selected from alkyls, alkenyls, halogen, substituted alkyls, aryls, arylhalides, alkoxy and halides. Preferably, the three groups are independently selected from halogen, mono or multicyclic (including halosubstituted) aryls, alkyls, and alkenyl compounds and mixtures thereof, preferred are alkenyl groups having 1 to 20 carbon atoms, alkyl groups having 1 to 20 carbon atoms, alkoxy groups having 1 to 20 carbon atoms and aryl groups having 3 to 20 carbon atoms (including substituted aryls). More preferably, the three groups are alkyls having 1 to 4 carbon groups, phenyl, napthyl or mixtures thereof. Even more preferably, the three groups are halogenated, preferably fluorinated, aryl groups. Most preferably, the neutral stoichiometric activator is trisperfluorophenyl boron or trisperfluoronaphthyl boron.

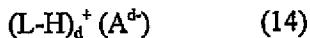
[00170] Ionic stoichiometric activator compounds may contain an active proton, or some other cation associated with, but not coordinated to, or only loosely coordinated to, the remaining ion of the ionizing compound. Such compounds and the like are described in European publications EP-A-0 570 982, EP-A-0 520 732, EP-A-0 495 375, EP-B1-0 500 944, EP-A-0 277 003 and EP-A-0 277 004, and U.S. Patent Nos. 5,153,157, 5,198,401, 5,066,741, 5,206,197, 5,241,025, 5,384,299 and 5,502,124 and U.S. Patent Application Serial No. 08/285,380, filed August 3, 1994, all of which are herein fully incorporated by reference.

[00171] Ionic catalysts can be preparedly reacting a transition metal compound with some neutral Lewis acids, such as $B(C_6F_5)_3$, which upon reaction with the hydrolyzable ligand (X) of the transition metal compound forms an anion, such as $([B(C_6F_5)_3(X)])^-$, which stabilizes the cationic transition metal species generated by the reaction. The catalysts can be, and preferably are, prepared with

activator components which are ionic compounds or compositions. However preparation of activators utilizing neutral compounds is also contemplated by this invention.

[00172] Compounds useful as an activator component in the preparation of the ionic catalyst systems used in the process of this invention comprise a cation, which is preferably a Bronsted acid capable of donating a proton, and a compatible non-coordinating anion which anion is relatively large (bulky), capable of stabilizing the active catalyst species (the Group 4 cation) which is formed when the two compounds are combined and said anion will be sufficiently labile to be displaced by olefinic diolefinic and acetylenically unsaturated substrates or other neutral Lewis bases such as ethers, nitriles and the like. Two classes of compatible non-coordinating anions have been disclosed in EPA 277,003 and EPA 277,004 published 1988: 1) anionic coordination complexes comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central charge-bearing metal or metalloid core, and 2) anions comprising a plurality of boron atoms such as carboranes, metallacarboranes and boranes.

[00173] In a preferred embodiment, the stoichiometric activators include a cation and an anion component, and may be represented by the following formula:



wherein L is a neutral Lewis base;

H is hydrogen;

$(L-H)^+$ is a Bronsted acid

A^{d-} is a non-coordinating anion having the charge d-

d is an integer from 1 to 3.

[00174] The cation component, $(L-H)_d^+$ may include Bronsted acids such as protons or protonated Lewis bases or reducible Lewis acids capable of protonating

or abstracting a moiety, such as an alkyl or aryl, from the bulky ligand metallocene containing transition metal catalyst precursor, resulting in a cationic transition metal species.

[00175] The activating cation $(L-H)_d^+$ may be a Bronsted acid, capable of donating a proton to the transition metal catalytic precursor resulting in a transition metal cation, including ammoniums, oxoniums, phosphoniums, silylums, and mixtures thereof, preferably ammoniums of methylamine, aniline, dimethylamine, diethylamine, N-methylaniline, diphenylamine, trimethylamine, triethylamine, N,N-dimethylaniline, methyldiphenylamine, pyridine, p-bromo N,N-dimethylaniline, p-nitro-N,N-dimethylaniline, phosphoniums from triethylphosphine, triphenylphosphine, and diphenylphosphine, oxoniums from ethers such as dimethyl ether diethyl ether, tetrahydrofuran and dioxane, sulfoniums from thioethers, such as diethyl thioethers and tetrahydrothiophene, and mixtures thereof. The activating cation $(L-H)_d^+$ may also be a moiety such as silver, tropylium, carbeniums, ferroceniums and mixtures, preferably carboniums and ferroceniums. Most preferably $(L-H)_d^+$ is triphenyl carbonium.

[00176] The anion component A^d include those having the formula $[M^{k+}Q_n]^d$ wherein k is an integer from 1 to 3; n is an integer from 2-6; $n - k = d$; M is an element selected from Group 13 of the Periodic Table of the Elements, preferably boron or aluminum, and Q is independently a hydride, bridged or unbridged dialkylamido, halide, alkoxide, aryloxide, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, and halosubstituted-hydrocarbyl radicals, said Q having up to 20 carbon atoms with the proviso that in not more than 1 occurrence is Q a halide. Preferably, each Q is a fluorinated hydrocarbyl group having 1 to 20 carbon atoms, more preferably each Q is a fluorinated aryl group, and most preferably each Q is a pentafluoryl aryl group. Examples of suitable A^d also include diboron compounds as disclosed in U.S. Pat. No. 5,447,895, which is fully incorporated herein by reference.

[00177] Illustrative, but not limiting examples of boron compounds which may be used as an activating cocatalyst in the preparation of the improved catalysts of this invention are tri-substituted ammonium salts such as:

trimethylammonium tetraphenylborate, triethylammonium tetraphenylborate,
tripropylammonium tetraphenylborate, tri(n-butyl)ammonium tetraphenylborate,
tri(t-butyl)ammonium tetraphenylborate, N,N-dimethylanilinium
tetraphenylborate,
N,N-diethylanilinium tetraphenylborate, N,N-dimethyl-(2,4,6-trimethylanilinium)
tetraphenylborate, tropillium tetraphenylborate,
triphenylcarbenium tetraphenylborate, triphenylphosphonium tetraphenylborate
triethylsilylium tetraphenylborate, benzene(diazonium)tetraphenylborate,
trimethylammonium tetrakis(pentafluorophenyl)borate, triethylammonium
tetrakis(pentafluorophenyl)borate, tripropylammonium
tetrakis(pentafluorophenyl)borate, tri(n-butyl)ammonium
tetrakis(pentafluorophenyl)borate, tri(sec-butyl)ammonium
tetrakis(pentafluorophenyl)borate, N,N-dimethylanilinium
tetrakis(pentafluorophenyl)borate, N,N-diethylanilinium
tetrakis(pentafluorophenyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium)
tetrakis(pentafluorophenyl)borate, tropillium tetrakis(pentafluorophenyl)borate,
triphenylcarbenium tetrakis(pentafluorophenyl)borate, triphenylphosphonium
tetrakis(pentafluorophenyl)borate, triethylsilylium
tetrakis(pentafluorophenyl)borate,
benzene(diazonium) tetrakis(pentafluorophenyl)borate, trimethylammonium
tetrakis-(2,3,4,6-tetrafluorophenyl) borate, triethylammonium tetrakis-(2,3,4,6-
tetrafluorophenyl)borate, tripropylammonium tetrakis-(2,3,4,6-
tetrafluorophenyl)borate, tri(n-butyl)ammonium tetrakis-(2,3,4,6-
tetrafluorophenyl)borate, dimethyl(t-butyl)ammonium tetrakis-(2,3,4,6-
tetrafluorophenyl)borate, N,N-dimethylanilinium tetrakis-(2,3,4,6-
tetrafluorophenyl)borate, N,N-diethylanilinium tetrakis-(2,3,4,6-

tetrafluorophenyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis-(2,3,4,6-tetrafluorophenyl)borate, tropillium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, triphenylcarbenium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, triphenylphosphonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, triethylsilylium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, benzene(diazonium) tetrakis-(2,3,4,6-tetrafluorophenyl)borate, trimethylammonium tetrakis(perfluoronaphthyl)borate, triethylammonium tetrakis(perfluoronaphthyl)borate, tri(n-butyl)ammonium tetrakis(perfluoronaphthyl)borate, tri(t-butyl)ammonium tetrakis(perfluoronaphthyl)borate, N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate, N,N-diethylanilinium tetrakis(perfluoronaphthyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(perfluoronaphthyl)borate, tropillium tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluoronaphthyl)borate, triphenylphosphonium tetrakis(perfluoronaphthyl)borate, triethylsilylium tetrakis(perfluoronaphthyl)borate, benzene(diazonium) tetrakis(perfluoronaphthyl)borate, trimethylammonium tetrakis(perfluorobiphenyl)borate, triethylammonium tetrakis(perfluorobiphenyl)borate, tripropylammonium tetrakis(perfluorobiphenyl)borate, tri(n-butyl)ammonium tetrakis(perfluorobiphenyl)borate, N,N-dimethylanilinium tetrakis(perfluorobiphenyl)borate, N,N-diethylanilinium tetrakis(perfluorobiphenyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(perfluorobiphenyl)borate, tropillium tetrakis(perfluorobiphenyl)borate, triphenylcarbenium tetrakis(perfluorobiphenyl)borate, triphenylphosphonium tetrakis(perfluorobiphenyl)borate, triethylsilylium tetrakis(perfluorobiphenyl)borate, triethylsilylium tetrakis(perfluorobiphenyl)borate,

benzene(diazonium) tetrakis(perfluorobiphenyl)borate, trimethylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triethylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, tripropylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, tri(n-butyl)ammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, tri(t-butyl)ammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, N,N-dimethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, N,N-diethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, tropillium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triphenylphosphonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triethylsilylium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, benzene(diazonium) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, and dialkyl ammonium salts such as: di-(i-propyl)ammonium tetrakis(pentafluorophenyl)borate, and dicyclohexylammonium tetrakis(pentafluorophenyl)borate; and additional tri-substituted phosphonium salts such as tri(o-tolyl)phosphonium tetrakis(pentafluorophenyl)borate, and tri(2,6-dimethylphenyl)phosphonium tetrakis(pentafluorophenyl)borate.

[00178] Most preferably, the ionic stoichiometric activator $(L-H)_d^+ (A^d)$ is N,N-dimethylanilinium tetra(perfluorophenyl)borate, N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate, N,N-dimethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triphenylcarbenium tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluorobiphenyl)borate, triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, or triphenylcarbenium tetra(perfluorophenyl)borate.

[00179] In one embodiment, an activation method using ionizing ionic compounds not containing an active proton but capable of producing a bulky ligand metallocene catalyst cation and their non-coordinating anion are also contemplated, and are described in EP-A- 0 426 637, EP-A- 0 573 403 and U.S. Patent No. 5,387,568, which are all herein incorporated by reference.

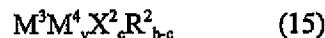
[00180] The term "non-coordinating anion" (NCA) means an anion which either does not coordinate to said cation or which is only weakly coordinated to said cation thereby remaining sufficiently labile to be displaced by a neutral Lewis base. "Compatible" non-coordinating anions are those which are not degraded to neutrality when the initially formed complex decomposes. Further, the anion will not transfer an anionic substituent or fragment to the cation so as to cause it to form a neutral four coordinate metallocene compound and a neutral by-product from the anion. Non-coordinating anions useful in accordance with this invention are those that are compatible, stabilize the metallocene cation in the sense of balancing its ionic charge at +1, yet retain sufficient lability to permit displacement by an ethylenically or acetylenically unsaturated monomer during polymerization. These types of cocatalysts sometimes use tri-isobutyl aluminum or tri-octyl aluminum as a scavenger.

[00181] Invention process also can employ cocatalyst compounds or activator compounds that are initially neutral Lewis acids but form a cationic metal complex and a noncoordinating anion, or a zwitterionic complex upon reaction with the invention compounds. For example, tris(pentafluorophenyl) boron or aluminum act to abstract a hydrocarbyl or hydride ligand to yield an invention cationic metal complex and stabilizing noncoordinating anion, see EP-A-0 427 697 and EP-A-0 520 732 for illustrations of analogous Group-4 metallocene compounds. Also, see the methods and compounds of EP-A-0 495 375. For formation of zwitterionic complexes using analogous Group 4 compounds, see U.S. Patents 5,624,878; 5,486,632; and 5,527,929.

[00182] When the cations of noncoordinating anion precursors are Bronsted acids such as protons or protonated Lewis bases (excluding water), or reducible Lewis acids such as ferrocenium or silver cations, or alkali or alkaline earth metal cations such as those of sodium, magnesium or lithium, the catalyst-precursor-to-activator molar ratio may be any ratio. Combinations of the described activator compounds may also be used for activation. For example, tris(perfluorophenyl) boron can be used with methylalumoxane.

Conventional-Type Cocatalysts (Activators)

[00183] Typically, conventional transition metal catalyst compounds excluding some conventional-type chromium catalyst compounds are activated with one or more of the conventional cocatalysts which may be represented by the formula:



wherein M^3 is a metal from Group 1 to 3 and 12 to 13 of the Periodic Table of Elements; M^4 is a metal of Group 1 of the Periodic Table of Elements; v is a number from 0 to 1; each X^2 is any halogen; c is a number from 0 to 3; each R^2 is a monovalent hydrocarbon radical or hydrogen; b is a number from 1 to 4; and wherein b minus c is at least 1. Other conventional-type organometallic cocatalyst compounds for the above conventional-type transition metal catalysts have the formula $M^3 R^2_k$, where M^3 is a Group IA, IIA, IIB or IIIA metal, such as lithium, sodium, beryllium, barium, boron, aluminum, zinc, cadmium, and gallium; k equals 1, 2 or 3 depending upon the valency of M^3 which valency in turn normally depends upon the particular Group to which M^3 belongs; and each R^2 may be any monovalent hydrocarbon radical.

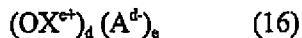
[00184] Non-limiting examples of conventional-type organometallic cocatalyst compounds useful with the conventional-type catalyst compounds described above include methylolithium, butyllithium, dihexylmercury, butylmagnesium, diethylcadmium, benzylpotassium, diethylzinc, tri-n-butylaluminum, diisobutyl ethylboron, diethylcadmium, di-n-butylzinc and tri-n-amylboron, and, in particular, the aluminum alkyls, such as tri-hexyl-aluminum, triethylaluminum, trimethylaluminum, and tri-isobutylaluminum. Other conventional-type cocatalyst compounds include mono-organohalides and hydrides of Group 2 metals, and mono- or di-organohalides and hydrides of Group 3 and 13 metals. Non-limiting examples of such conventional-type cocatalyst compounds include di-isobutylaluminum bromide, isobutylboron dichloride, methyl magnesium chloride, ethylberyllium chloride, ethylcalcium bromide, di-isobutylaluminum hydride, methylcadmium hydride, diethylboron hydride, hexylberyllium hydride, dipropylboron hydride, octylmagnesium hydride, butylzinc hydride, dichloroboron hydride, di-bromo-aluminum hydride and bromocadmium hydride. Conventional-type organometallic cocatalyst compounds are known to those in the art and a more complete discussion of these compounds may be found in U.S. Patent Nos. 3,221,002 and 5,093,415, which are herein fully incorporated by reference.

Additional Activators

[00185] Other activators include those described in PCT publication WO 98/07515 such as tris (2, 2', 2''- nonafluorobiphenyl) fluoroaluminate, which publication is fully incorporated herein by reference. Combinations of activators are also contemplated by the invention, for example, alumoxanes and ionizing activators in combinations, see for example, EP-B1 0 573 120, PCT publications WO 94/07928 and WO 95/14044 and U.S. Patent Nos. 5,153,157 and 5,453,410 all of which are herein fully incorporated by reference.

[00186] Other suitable activators are disclosed in WO 98/09996, incorporated herein by reference, which describes activating bulky ligand metallocene catalyst compounds with perchlorates, periodates and iodates including their hydrates. WO 98/30602 and WO 98/30603, incorporated by reference, describe the use of lithium (2,2'-bisphenyl-dtrimethylsilicate)•4THF as an activator for a bulky ligand metallocene catalyst compound. WO 99/18135, incorporated herein by reference, describes the use of organo-boron-aluminum activators. EP-B1-0 781 299 describes using a silylum salt in combination with a non-coordinating compatible anion. Also, methods of activation such as using radiation (see EP-B1-0 615 981 herein incorporated by reference), electro-chemical oxidation, and the like are also contemplated as activating methods for the purposes of rendering the neutral bulky ligand metallocene catalyst compound or precursor to a bulky ligand metallocene cation capable of polymerizing olefins. Other activators or methods for activating a bulky ligand metallocene catalyst compound are described in for example, U.S. Patent Nos. 5,849,852, 5,859,653 and 5,869,723 and WO 98/32775, WO 99/42467 (dioctadecylmethyldiammonium-bis(tris(pentafluorophenyl)borane) benzimidazolide), which are herein incorporated by reference.

[00187] Another suitable ion forming, activating cocatalyst comprises a salt of a cationic oxidizing agent and a noncoordinating, compatible anion represented by the formula:



wherein OX^{e+} is a cationic oxidizing agent having a charge of $e+$; e is an integer from 1 to 3; and A^- , and d are as previously defined. Examples of cationic oxidizing agents include: ferrocenium, hydrocarbyl-substituted ferrocenium, Ag^+ , or Pb^{2+} . Preferred embodiments of A^d are those anions previously defined with

respect to the Bronsted acid containing activators, especially tetrakis(pentafluorophenyl)borate.

[00188] It is within the scope of this invention that catalyst compounds can be combined one or more activators or activation methods described above. For example, a combination of activators have been described in U.S. Patent Nos. 5,153,157 and 5,453,410, European publication EP-B1 0 573 120, and PCT publications WO 94/07928 and WO 95/14044. These documents all discuss the use of an alumoxane and an ionizing activator with a bulky ligand metallocene catalyst compound.

The Choice of Transition Metal Catalyst Components

[00189] The catalyst system of this invention comprises two or more transition metal compounds as described above. At least one of the compounds must be capable of producing a crystalline poly-alpha-olefin, preferably isotactic polypropylene or syndiotactic polypropylene, having a crystallinity of 40% or more. The other compound must be capable of producing an amorphous poly-alpha-olefin, preferably atactic polypropylene, having a crystallinity of 20% or less.

[00190] The choice of transition metal component for the crystalline polymer fraction is a subset of the transition metal component of equations 8-9. This preferred component is illustrated in equation 17: